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(71) Applicant: SHOWA DENKO KABUSHIKI KAISHA
13-9, Shiba Daimon 1-chome
Minato-ku, Tokyo 105(JP)

(72) Inventor: Murofushi, Katsumi, c/o Showa Denko K.K.
Kagakuhin Kenkyusho, 5-1, Ohgimachi
Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)
Inventor: Hosoda, Yoshikazu, c/o Showa Denko K.K.
Kagakuhin Kenkyusho, 5-1, Ohgimachi
Kawasaki-ku, Kawasaki-shi, Kanagawa(JP)

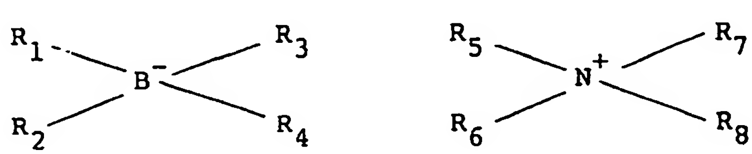
(74) Representative: Strehl, Schübel-Hopf, Groening
Maximilianstrasse 54 Postfach 22 14 55
W-8000 München 22(DE)

(54) Near infrared polymerization initiator.

(57) A near infrared polymerization initiator comprising a near infrared ray-absorbing cationic dye showing absorptions in the near infrared region, which is represented by the following general formula (1):

$D^{+}.A^{-}$ (1)

wherein D^{+} represents a cationic dyestuff having absorptions in the near infrared region, and A^{-} represents an anion,
and at least one member selected from the group consisting of boron-containing sensitizers represented by the following general formula (2):



(2)

wherein R_1, R_2, R_3 and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic, or saturated or unsaturated heterocyclic group, with the proviso that at least one of R_1, R_2, R_3 and R_4 represents an alkyl group having 1 to 8 carbon atoms, and R_5, R_6, R_7 and R_8 independently represent a hydrogen atom or an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, alicyclic or saturated or unsaturated heterocyclic group, and organic peroxides.

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NEAR INFRARED POLYMERIZATION INITIATOR

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a polymerization initiator capable of initiating polymerization of at least one ethylenically unsaturated polymerizable monomer or oligomer with near infrared rays at a high sensitivity.

(2) Description of the Related Art

Photopolymerization is widely utilized in various fields; for example, for curing a coating film, forming a planographic printing plate, a resin letterpress printing plate and a printed circuit board, preparing a photoresist and a photomask, and making a black-and-white or color transfer sheet and a coloring sheet. Furthermore, a photopolymerizable composition is used in the field of the dentistry. In each case, however, photopolymerization is effected with ultraviolet rays or visible rays, and a polymerization by near infrared rays has not been developed.

In general, the photopolymerizable composition comprises an ethylenically unsaturated compound and a photopolymerization initiator (see, for example, Japanese Unexamined Patent Publication No. 59-138203, Japanese Unexamined Patent Publication No. 63-162769 and Japanese Unexamined Patent Publication No. 64-72150). Japanese Unexamined Patent Publication No. 63-162769 discloses a photopolymerizable composition in which a vinyl compound is cured in the presence of an amine such as N,N-dimethylaniline by using an α-ketocarbonyl compound as the photopolymerization initiator under irradiation with ultraviolet rays and visible rays, and such photopolymerizable compositions are used as a tooth filler and a tooth sealant, for the production of a tooth crown and an artificial tooth bridge, and for the production of artificial teeth (see, for example, Japanese Unexamined Patent Publication No. 63-99858, Japanese Unexamined Patent Publication No. 63-189144 and Japanese Unexamined Patent Publication No. 63-203151). Furthermore, serious attempts have been made to develop an ultraviolet ray-curable ink as a photopolymerizable composition (see, for example, Japanese Unexamined Patent Publication No. 01-229084, Japanese Unexamined Patent Publication No. 01-271469 and Japanese Unexamined Patent Publication No. 02-22370).

Nevertheless, since visible rays are used for these photopolymerizable compositions, the light transmission is adversely affected by the hue of the composition or the filler, and the degree of curing is changed according to the hue or the amount added of the filler.

SUMMARY OF THE INVENTION

Therefore, a primary object of the present invention is to provide a polymerization initiator capable of initiating a polymerization at a high sensitivity with near infrared rays, which are not influenced by the hue of the photopolymerizable composition or the filler.

To solve this problem, investigations were made into a photopolymerization initiator comprising a specific near infrared ray-absorbing cationic dye and a boron-containing sensitizer and/or an organic peroxide in combination, and as a result, it was found that a spectrally sensitized polymerization initiator capable of initiating polymerization at a high sensitivity with near infrared rays can be obtained. The present invention is based on this finding.

More specifically, in accordance with the present invention, there is provided a near infrared polymerization initiator comprising a near infrared ray-absorbing cationic dye showing absorptions in the near infrared region, which is represented by the following general formula (1):

$$D^{+}.A^{-} \quad (1)$$

wherein D^{+} represents a cationic dyestuff having absorptions in the near infrared region, and A^{-} represents an anion,
and at least one member selected from the group consisting of boron-containing sensitizers represented by the following general formula (2):

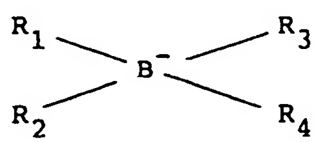
(2)

wherein R_1, R_2, R_3 and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic, or saturated or unsaturated heterocyclic group, with the proviso that at least one of R_1, R_2, R_3 and R_4 represents an alkyl group having 1 to 8 carbon atoms, and R_5, R_6, R_7 and R_8 independently represent a hydrogen atom or an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, alicyclic or saturated or unsaturated heterocyclic group,
and organic peroxides.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymerization initiator of the present invention is capable of initiating polymerization at a high sensitivity with near infrared rays having a wavelength of at least 700 nm. A photopolymerizable composition that can be polymerized with near infrared rays can be obtained by adding the near infrared photopolymerization initiator to a free-radical addition-polymerizable or crosslinkable compound, or a mixture of this compound with an organic filler, an inorganic filler or a composite filler thereof or with a colorant such as a coloring dye or a pigment.

As the specific cationic dyestuff constituting the near infrared ray-absorbing cationic dye used in the near infrared photopolymerization initiator of the present invention, there can be mentioned cyanine, triarylmethane, aminium and diimonium dyestuffs. As the anion, there can be mentioned halogen anions, ClO_4^-, PF_6^-, BF_4^-, SbF_6^-, $CH_3SO_3^-$, $F_3CSO_3^-$, $C_6H_4SO_3^-$, $CH_3C_6H_4SO_3^-$, $HOC_6H_4SO_3^-$, $ClC_6H_4SO_3^-$, and borate anions represented by the following general formula (3);



(3)

wherein R_1, R_2, R_3 and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic or saturated or unsaturated heterocyclic group, with the proviso that at least one of R_1, R_2, R_3 and R_4 represents an alkyl group having 1 to 8 carbon atoms.

As the borate anion, triphenylbutyl borate anion and trianisylbutyl borate anion are especially preferable. Examples of the near infrared ray-absorbing cationic dye used in the present invention are shown in Table 1.

Table 1

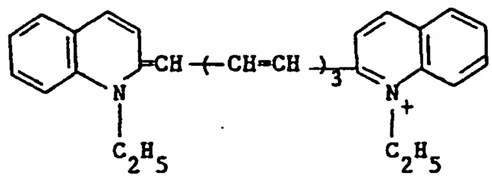
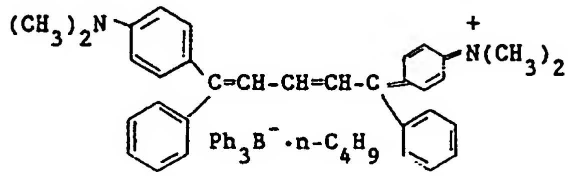
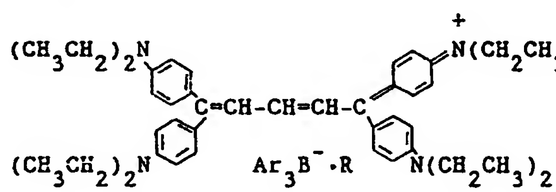
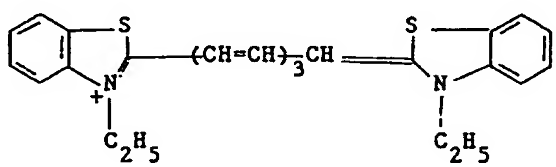
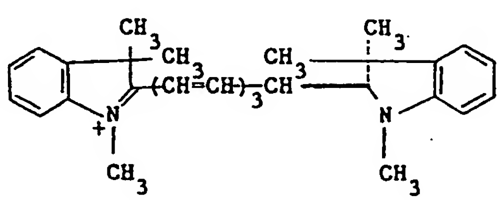
Dye No.	Structure	R	Ar	λ max (TMPT)
1	 $Ph_3B^- \cdot n\text{-}C_4H_9$			820nm
2				830nm
3-A		n-butyl	phenyl	822nm
3-B		n-hexyl	anisyl	822nm
3-C		n-octyl	phenyl	822nm
4	 $Ph_3B^- \cdot n\text{-}C_4H_9$			768nm
-A	 $Ar_3B^- \cdot R$	n-butyl	phenyl	748nm
5-B		n-hexyl	anisyl	748nm
-C		n-octyl	phenyl	748nm

Table 1 (continued)

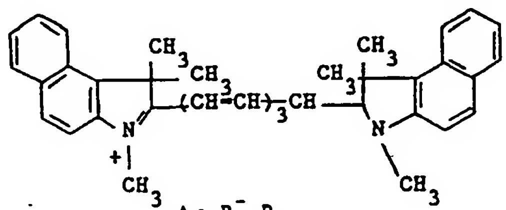
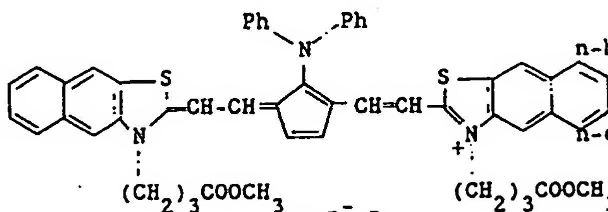
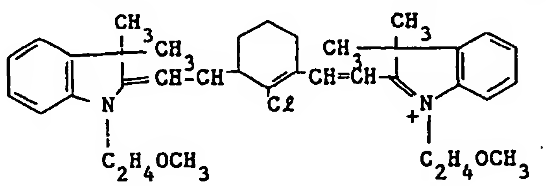
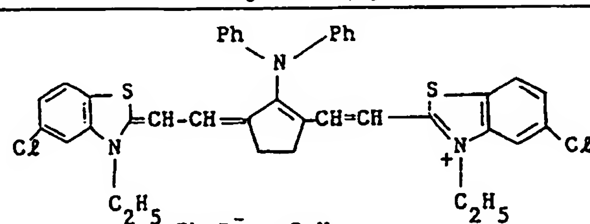
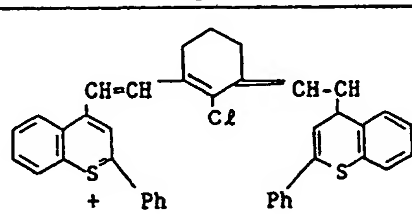
Dye No.	Structure	R	Ar	λ max (TMPT)
6-A	 $Ar_3B^-\cdot R$	n-butyl	phenyl	785nm
6-B		n-hexyl	anisyl	785nm
6-C		n-octyl	phenyl	785nm
7-A	 $Ar_3B^-\cdot R$	n-butyl	phenyl	828nm
7-B		n-hexyl	anisyl	828nm
7-C		n-octyl	phenyl	828nm
8	 $Ph_3B^-\cdot n\text{-}C_4H_9$			787nm
9	 $Ph_3B^-\cdot n\text{-}C_4H_9$			819nm
10	 $Ph_3B^-\cdot n\text{-}C_4H_9$			1080nm

Table 1 (continued)

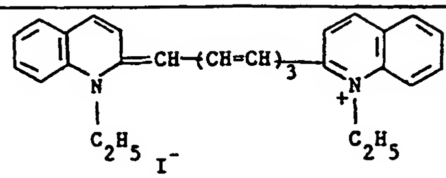
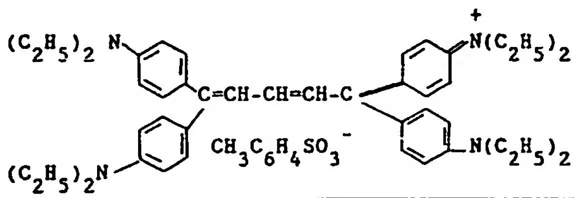
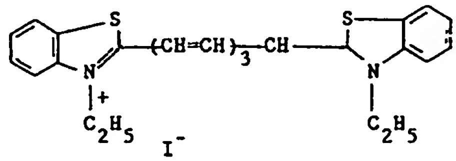
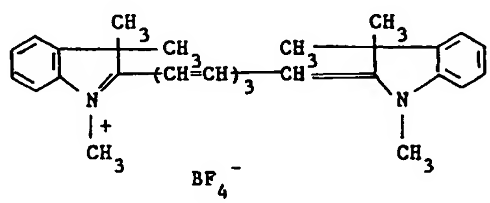
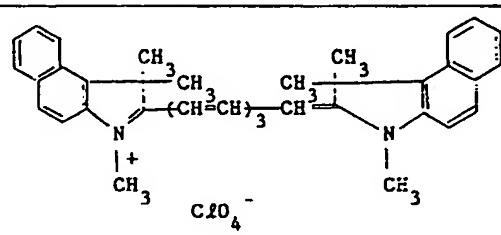
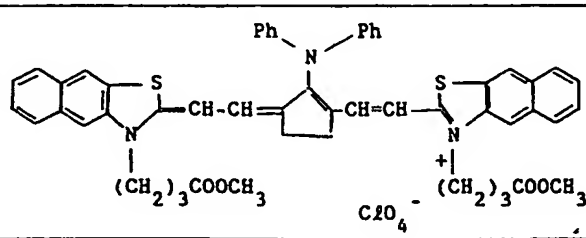
Dye No.	Structure	λ max (TMPT)
11		820nm
12		822nm
13		768nm
14		748nm
15		785nm
16		828nm

Table 1 (continued)

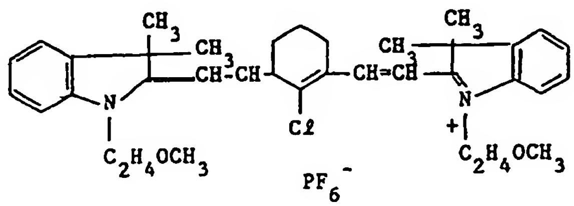
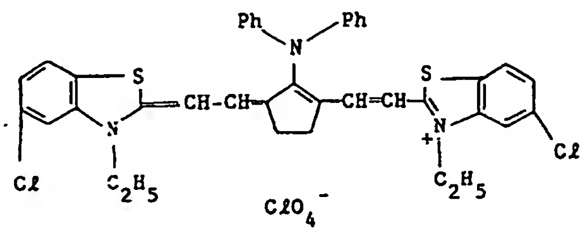
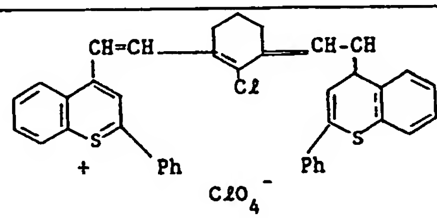
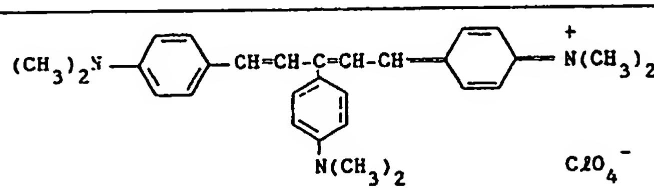
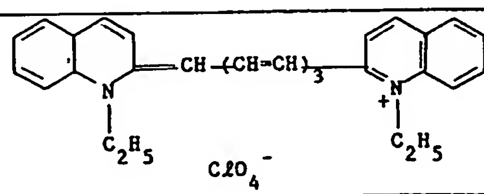
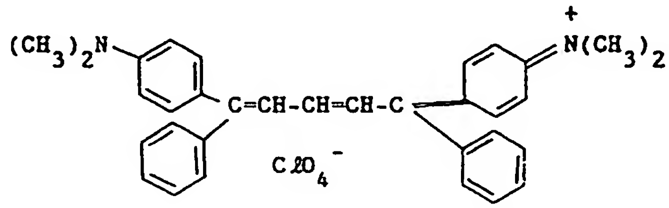
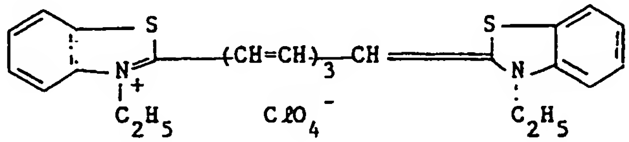
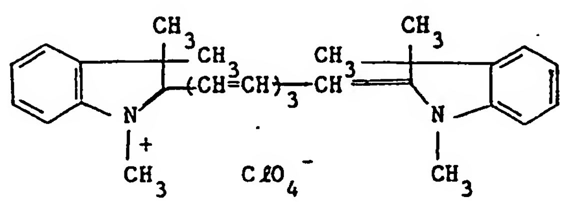
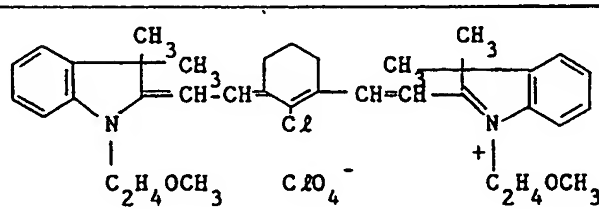
Dye No. (TMPT)	Structure	λ max (TMPT)
17		787nm
18		819nm
19		1080nm
20		770nm
21		820nm

Table 1 (continued)

Dye No.	Structure	λ max (TMPT)
22		830nm
23		768nm
24		748nm
25		787nm

Note

λ: absorption wavelength

TMPT: trimethylolpropane trimethacrylate

Ph: phenyl group

Preferably, these dyes are used in combination with an oxygen scavenger capable of absorbing oxygen in the free radical chain transfer process and a chain transfer agent acting as an active hydrogen donor. As examples of the oxygen scavenger, there can be mentioned, for example, phosphines, phosphites, phosphonates, stannous salts and other compounds that can be easily oxidized by oxygen. As the chain transfer agent, there can be mentioned, for example, N-phenylglycine, N-substituted N-phenylglycines such as methacryloxy-β-hydroxypropyl-N-phenylglycine, trimethylbarbituric acid, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, and N,N-dialkylanilines. Examples of the N,N-dialkylaniline are those in which at least one of ortho-, meta- and para-positions is substituted with an alkyl group, a phenyl group, an acetyl group, an ethoxycarbonyl group, a carbonyl group, a carboxylate group, a silyl group, an alkoxy group, a phenoxy group, an acetyloxy group, a hydroxyl group or a halogen atom. Ah N,N-dialkylaniline having the ortho-position substituted with an alkyl group is especially preferably used. For example, there can be mentioned

2,6-diisopropyl-N,N-dimethylaniline, 2,6-diethyl-N,N-dimethylaniline, N,N,2,4,6-pentamethylaniline and p-t-butyl-N,N-dimethylaniline.

The boron-containing sensitizer used in the present invention is a quaternary ammonium-borate complex represented by the general formula (2). As preferable examples, there can be mentioned tetramethylammonium n-butyltriphenyl borate, tetramethylammonium n-butyltrianisyl borate, tetramethylammonium n-octyltriphenyl borate, tetramethylammonium n-octyltrianisyl borate, tetraethylammonium n-butyltriphenyl borate, tetraethylammonium n-butyltrianisyl borate, trimethylhydrogenammonium n-butyltriphenyl borate, triethylhydrogenammonium n-butyltriphenyl borate, tetrahydrogeneammonium n-butyltriphenyl borate, tetramethylammonium tetrabutyl borate and tetraethylammonium tetrabutyl borate.

Any of organic peroxides customarily used can be used as the organic peroxide. For example, there can be mentioned diacyl peroxides such as diacetyl peroxide, dilauroyl peroxide, dibenzoyl peroxide, p,p'-dichlorodibenzoyl peroxide, p,p'-dimethoxydibenzoyl peroxide, p,p'-dimethyldibenzoyl peroxide and p,p'-dinitrodibenzoyl peroxide, hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide and 2,5-dimethylhexane-2,5-dihydroperoxide, ketone peroxides such as methylethylketone peroxide, and peroxycarbonates such as t-butylperoxide benzoate and 3,3',4,4'-tetra-(t-butylperoxycarbonyl)benzophenone. Of these peroxides, dibenzoyl peroxide and 3,3',4,4'-tetra-(t-butylperoxycarbonyl)benzophenone are preferably used.

The free-radical addition polymerizable or crosslinkable compound to which the polymerization initiator of the present invention can be applied includes all of customarily used ethylenically unsaturated compounds, especially acrylic acid and methacrylic acid esters of monohydric alcohols and polyhydric alcohols, and 4-(meth)acryloyloxyl group-containing aromatic polycarboxylic acids and anhydrides thereof. So-called urethane acrylate and methacrylate are included in the above-mentioned esters.
Furthermore,
2,2-bis[4-(3-methacryloxy-2-hydropoxy)-phenyl]propane, which is a reaction product known from U. S. Patent No. 3,066,112,
di(methacryloxyethyl)trimethylhexamethylenediurethane, 2,2-bis(4-methacryloxypolyethoxyphenyl)propane, tetramethylolmethane trimethacrylate, tetramethylolmethane tetramethacrylate, dipentaerythritolhexaacrylate, dipentaerythritolhexamethacrylate, 4-(meth)acryloyloxymethoxycarbonylphthalic acid, an anhydride thereof, 4-(meth)acryloyloxyethoxycarbonylphthalic acid and an anhydride thereof are meant.

The filler that can be used in combination with the above-mentioned ethylenically unsaturated compound includes organic fillers, inorganic fillers and composite fillers thereof. A fine pulverization product of a polymer of an ethylenically unsaturated compound as mentioned above can be used as the organic filler. As the inorganic filler, there can be mentioned powders of silica, silica-alumina, alumina, quartz, glass, calcium carbonate, kaolin, talc, mica, aluminum sulfate, barium sulfate, calcium sulfate, titanium oxide and calcium phosphate, and fillers formed by coating the surfaces of these powders with polyfunctional (meth)-acrylate monomers or silane coupling agents. As the composite filler, there can be mentioned a product obtained by mixing an inorganic filler as mentioned above with an ethylenically unsaturated compound as mentioned above, polymerizing and curing the mixture and finely pulverizing the formed polymer.

Not only commercially available coloring dyes and pigments but also known dyes and pigments disclosed in various literature references (for example, "Handbook of Dyes" compiled by the Association of Organic Synthetic Chemistry and published in 1970 and "Newest Pigment Handbook" compiled by the Japanese Pigment Technical Association and published in 1976) can be used as the colorant in the present invention.

Preferably, the near infrared photopolymerization initiator of the present invention contains the near infrared ray-absorbing cationic dye in an amount of 0.01 to 10% by weight, especially 0.1 to 5% by weight, based on the ethylenically unsaturated compound, and the boron-containing sensitizer and/or the organic peroxide is contained in an amount of 0.01 to 10% by weight, especially 0.1 to 5% by weight, per % by weight of the near infrared ray-absorbing cationic dye. Furthermore, an oxygen scavenger and a chain transfer agent can be added in amounts similar to the amount of the near infrared ray-absorbing cationic dye.

The photopolymerization initiator of the present invention is utilized in the fields where photopolymerization is conducted, for example, for photography, screen printing, sheet printing, planography, letterpress printing and metal surface processing, for the preparation of inks and printed circuit boards, for the formation of photoresists, photomasks, black-and-white and color transfer sheets and coloring sheets, for the production of toners for copying machines and encapsulated toners for copying machines, for the curing of paints, adhesives and unsaturated polyesters, for crosslinking of rubbers, and for the modification and crosslinking of polyolefins. A composition comprising this photopolymerization initiator, an ethylenically unsaturated compound, and a leuco dye or a coloring dye having an absorption in the visible region can be used for the formation of a black-and-white or color transfer sheet or a coloring sheet. The composition can

be used when enclosed in microcapsules. Furthermore, the photopolymerization initiator of the present invention can be used for a dental filling composition for a denture or dental prosthesis, a dental covering or adhesive composition, and other dental treatment compositions. Note, the application ranges of the photopolymerization initiator of the present invention are not limited by the foregoing examples.

A specific example of the application to a printing ink will now be described. A monomer or prepolymer having an ethylenically unsaturated group, which is usually used as the active vehicle, is kneaded with the near infrared photopolymerization initiator of the present invention and a pigment and the obtained near infrared ray-curable ink is printed to a thickness of 5 μm on an aluminum foil sheet used for packaging cosmetics and foods. Then, the coated aluminum foil sheet is irradiated with rays from an infrared ray irradiation apparatus, whereby the ink is dry-fixed to the aluminum foil sheet having no permeability and no drying property.

As an example of the application to a dental composition, there can be mentioned a treatment of a decayed portion of a molar tooth or front tooth of a patient. More specifically, the decayed portion is removed by a dental drill and the tooth is treated with an etching solution, a dental composition comprising the near infrared polymerization initiator is filled in the cavity, and the composition is cured by irradiation with near infrared rays by using a near infrared ray irradiation apparatus, whereby the treatment is accomplished.

According to the present invention, there is provided a polymerization initiator comprising a near infrared ray-absorbing cationic dye and a boron-containing sensitizer and/or an organic peroxide, which is capable of initiating polymerization at a high sensitivity with near infrared rays, not influenced by the hue of a photopolymerizable composition or a filler.

The present invention will now be described in detail with reference to the following examples that by no means limit the scope of the invention.

Examples 1 through 8

A pasty mixture comprising 4 g of 2,2'-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl] propane, 2 g of trimethylolpropane trimethacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 30 g of fine silica (particle size smaller than 10 μm; average particle size of 5 μm), a near infrared ray-absorbing cationic dye shown in Table 2, a boron-containing sensitizer shown in Table 2 and 0.04 g of N,N,2,4,6-pentamethylaniline was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm) and the surface of the filled paste was covered with a polyester film to from a sample.

Examples 9 through 12

A pasty mixture comprising 4 g of 2,2-di(methacryloxy)trimethylhexamethylene diurethane, 2 g of trimethylolpropane triacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 1 g of lithium aluminum silicate (particle size smaller than 10 μm; average particle size of 5 μm), 29 g of aluminum oxide, a near infrared ray-absorbing cationic dye shown in Table 2, a boron-containing sensitizer shown in Table 2 and 0.04 g of N,N,2,4,6-pentamethylaniline was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled paste was covered with a polyester film to form a sample.

Examples 13 through 15

A mixture comprising 6 g of trimethylolpropane trimethacrylate, 4 g of triethylene glycol dimethacrylate, a near infrared ray-absorbing cationic dye shown in Table 2, a boron-containing sensitizer shown in Table 2, 0.04 g of N,N,2,4,6-pentamethylaniline and a colorant (supplied by Orient Kagaku Kogyo) shown in Table 2 was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was covered with a polyester film to form a sample.

Examples 16 through 18

A mixture comprising 6 g of trimethylolpropane trimethacrylate, 4 g of triethylene glycol dimethacrylate, an infrared ray-absorbing cationic dye shown in Table 2, a boron-containing sensitizer shown in Table 2, 0.03 g of N-phenylglycine and a colorant (supplied by Orient Kagaku Kogyo) shown in Table 2 was filled in a mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was

covered with a polyester film to form a sample.

Comparative Example 1

By using the same near infrared ray-absorbing cationic dye as used in Example 1, a sample was prepared in the same manner as described in Example 1 except that a boron-containing sensitizer was not used, as shown in Table 2.

Comparative Example 2

By using the same infrared ray-absorbing cationic dye as used in Example 7, a sample was prepared in the same manner as described in Example 7 except that a boron-containing sensitizer was not used, as shown in Table 2.

Comparative Example 3

A sample was prepared in the same manner as described in Example 1 except that camphorquinone and hydroquinone monomethyl ether, heretofore used for a visible ray polymerization type resin, were used instead of the near infrared-absorbing cationic dye and boron-containing sensitizer used in Example 1, as shown in Table 2.

Table 2

	Photopolymerization Initiator (Dye No. in Table 1)	Amount (% by weight)
Example 1	dye 5A TEAPB	0.1 0.01
Example 2	dye 5A TEAPB	0.1 0.3
Example 3	dye 5A TEAPB	0.1 0.5
Example 4	dye 3A TMAPB	0.1 0.3
Example 5	dye 5B TMAPB	0.1 0.3
Example 6	dye 6C TMAPB	0.1 0.3
Example 7	dye 12 TMAPB	0.1 0.3
Example 8	dye 16 TMAPB	0.1 0.3
Example 9	dye 3B TMAAB	0.1 0.3
Example 10	dye 6C TMAAB	0.1 0.3
Example 11	dye 7A TMHPB	0.1 0.3
Example 12	dye 18 TMAAB	0.1 0.3
Example 13	dye 3A TMAPB colorant SO Red 1	0.1 0.3 10.0

Table 2 (continued)

	Photopolymerization Initiator (Dye No. in Table 1)	Amount (% by weight)
Example 14	dye 7B TMAPB colorant SO Cyane 1	0.1 0.3 10.0
Example 15	dye 16 TMAPB colorant SO Red 1	0.1 0.3 10.0
Example 16	dye 3A TMAPB colorant SO Red 1	0.1 0.3 10.0
Example 17	dye 7B TMAPB colorant SO Cyane 1	0.1 0.3 10.0
Example 18	dye 12 TMAPB colorant SO Red 1	0.1 0.3 10.0
Comparative Example 1	dye 5A	0.1
Comparative Example 2	dye 12	0.1
Comparative Example 3	camphorquinone hydroquinone monomethyl ether	0.1 0.02

Note

TMAPB: tetramethylammonium n-butyltriphenyl borate

TEAPB: tetraethylammonium n-butyltriphenyl borate

TMAAB: tetramethylammonium n-butyltrianisyl borate

TMHPB: tetramethylhydrogenammonium n-butyltriphenyl borate

Each of the samples obtained in the foregoing examples and comparative examples was irradiated with a semiconductor laser having a wavelength of 830 nm, at an intensity of 200 mW for 10 seconds, and then the irradiated samples were immersed in ethanol for 1 hour to remove the unpolymerized component. Thereafter, with respect to each of samples of Examples 1 through 18 and Comparative Examples 1 through 3, the polymerizability and hue were evaluated, and the results are shown in Table 3.

Table 3

	Hue after irradiation	Polymerizability
Example 1	milky white	O
Example 2	milky white	O
Example 3	milky white	O
Example 4	milky white	O
Example 5	milky white	O
Example 6	milky white	O
Example 7	milky white	O
Example 8	milky white	O
Example 9	milky white	O
Example 10	milky white	O
Example 11	milky white	O
Example 12	milky white	O
Example 13	red	O
Example 14	blue	O
Example 15	red	O
Example 16	red	O
Example 17	blue	O
Example 18	red	O
Comparative Example 1	milky white	Δ
Comparative Example 2	blue	×
Comparative Example 3	milky white	×

Note

O: irradiated portion was completely polymerized

Δ: unpolymerized part remained in irradiated portion

×: irradiated portion was not polymerized

Examples 19 through 24

A pasty mixture comprising 4 g of 2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane, 2 g of trimethylolpropane trimethacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 30 g of fine silica (particle size smaller than 10 μm; average particle size of 5 μm), a near infrared ray-absorbing dye shown in Table 4, an organic peroxide shown in Table 4 and 0.04 g of 2,6-diisopropyl-N,N-dimethylaniline was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was covered with a polyester film to form a sample.

Examples 25 and 26

A pasty mixture comprising 4 g of 2,2-di(methacryloxyethyl)trimethylhexamethylenediurethane, 2 g of trimethylolpropane triacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 1 g of lithium aluminum silicate (particle size smaller than 10 μm; average particle size of 5 μm), 29 g of aluminum oxide, a near infrared ray-absorbing dye shown in Table 4 and an organic peroxide shown in Table 4 was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was covered with a polyester film to form a sample.

Examples 27 and 28

A pasty mixture comprising 4 g of 2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane, 2 g of trimethylolpropane trimethacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 30 g of fine silica (particle size smaller than 10 μm; average particle size of 5 μm), a near infrared ray-absorbing dye shown in Table 4, an organic peroxide shown in Table 4 and 0.04 g of 2,6-diisopropyl-N,N-dimethylaniline was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was covered with a polyester film to form a sample.

Comparative Example 4

A sample was prepared in the same manner as described in Example 19 except that camphorquinone and hydroquinone monomethyl ether, heretofore used for a visible ray polymerization type resin, were used instead of the near infrared-absorbing cationic dye and organic peroxide used in Example 19, as shown in Table 4.

Table 4

	Polymerization Initiator	Amount (% by weight)
Example 19	dye 5A TBBPB	0.1 0.01
Example 20	dye 5A TBBPB	0.1 0.3
Example 21	dye 5A TBBPB	0.1 0.5
Example 22	dye 5B TBBPB	0.1 0.3
Example 23	dye 6C TBBPB	0.1 0.3
Example 24	dye 7A TBBPB	0.1 0.3
Example 25	dye 24 BPO	0.1 0.3
Example 26	dye 16 BPO	0.1 0.3
Example 27	dye 5A BPO	0.1 0.3
Example 28	dye 7A BPO	0.1 0.3
Comparative Example 4	camphorquinone hydroquinone monomethyl ether	0.1 0.02

Note

TBBPB: 3,3', 4,4'-tetra-(t-butyl-peroxycarbonyl) benzophenone

BPO: dibenzoyl peroxide

Each of the samples obtained in the foregoing examples and comparative example was irradiated with a semiconductor laser having a wavelength of 830 nm, at an intensity of 200 mW for 20 seconds, and then the irradiated samples were immersed in ethanol for 1 hour to remove the unpolymerized component. Thereafter, with respect to each of samples of Examples 19 through 28 and Comparative Example 4, the polymerizability and hue were evaluated, and the results are shown in Table 5.

Table 5

	Hue after irradiation	Polymerizability
Example 19	milky white	O
Example 20	milky white	O
Example 21	milky white	O
Example 22	milky white	O
Example 23	milky white	O
Example 24	milky white	O
Example 25	milky white	O
Example 26	milky white	O
Example 27	milky white	O
Example 28	milky white	O
Comparative Example 4	milky white	×

Note

O: irradiated portion was completely polymerized

x: irradiated portion was not polymerized

Examples 29 through 31

A pasty mixture comprising 4 g of 2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane, 2 g of trimethylolpropane trimethacrylate, 1 g of triethylene glycol dimethacrylate, 3 g of diethylene glycol dimethacrylate, 30 g of fine silica (particle size smaller than 10 μm; average particle size of 5 μm), a near infrared ray-absorbing cationic dye shown in Table 6, a boron-containing sensitizer shown in Table 6 and an organic peroxide shown in Table 6 was filled in a stainless steel mold (having an inner diameter of 6 mm and a height of 8 mm), and the surface of the filled mixture was covered with a polyester film to form a sample.

Table 6

	Photopolymerization Initiator (Dye No. in Table 1)	Amount (% by weight)
Example 29	dye 3A TMAPB TBBPB	0.1 0.3 0.3
Example 30	dye 7B TMAPB MEKP	0.1 0.3 0.3
Example 31	dye 12 TMAPB TBBPB	0.1 0.3 0.3

Note

TMAPB: tetramethylammonium n-butyltriphenyl borate

TBBTB: 3,3′,4,4′-tetra(t-butylperoxycarbonyl)benzophenone

MEKP: methylethylketone peroxide

Each of the samples obtained in the foregoing examples was irradiated with a semiconductor laser having a wavelength of 830 nm, at an intensity of 200 mW for 10 seconds, and then the irradiated samples were immersed in ethanol for 1 hour to remove the unpolymerized component. Thereafter, with respect to each of samples of Examples 29 through 31, the polymerizability and hue were evaluated, and the results are shown in Table 7.

Table 7

	Hue after Irradiation	Polymerizability
Example 29	milky white	O
Example 30	milky white	O
Example 31	milky white	O

Note

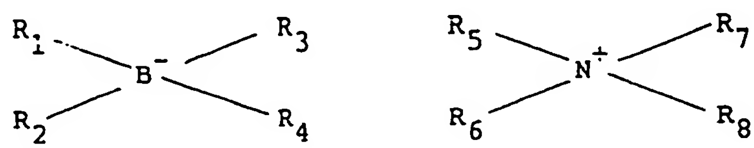
O: irradiated portion was completely polymerized

Claims

1. A near infrared polymerization initiator comprising a near infrared ray-absorbing cationic dye showing absorptions in the near infrared region, which is represented by the following general formula (1):

$D^{+}.A^{-}$ (1)

wherein D^+ represents a cationic dyestuff having absorptions in the near infrared region, and A^- represents an anion,
and at least one member selected from the group consisting of boron-containing sensitizers represented by the following general formula (2):

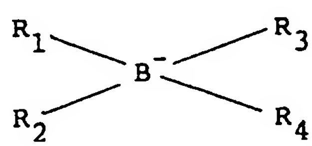


(2)

wherein R_1, R_2, R_3 and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic, or saturated or unsaturated heterocyclic group, with the proviso that at least one of R_1, R_2, R_3 and R_4 represents an alkyl group having 1 to 8 carbon atoms, and R_5, R_6, R_7 and R_8 independently represent a hydrogen atom or an alkyl, aryl, allyl, alkaryl, aralkyl, alkenyl, alkynyl, alicyclic or saturated or unsaturated heterocyclic group,
and organic peroxides.

2. An initiator as claimed in claim 1, wherein the cationic dyestuff is selected from cyanine, triarylmethane, aminium and diimonium dyestuffs.

3. An initiator as claimed in claim 1 or 2, wherein the anion is selected from halogen anions, ClO_4^-, PF_6^-, BF_4^-, SbF_6^-, $CH_3SO_3^-$, $F_3CSO_3^-$, $C_6H_4SO_3^-$, $CH_3C_6H_4S_3^-$, $HOC_6H_4SO_3^-$, $ClC_6H_4SO_3^-$, and borate anions represented by the following general formula (3);

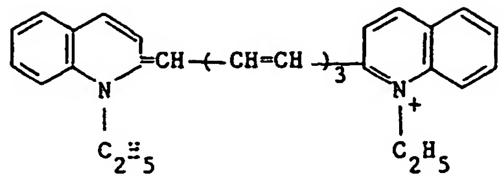


(3)

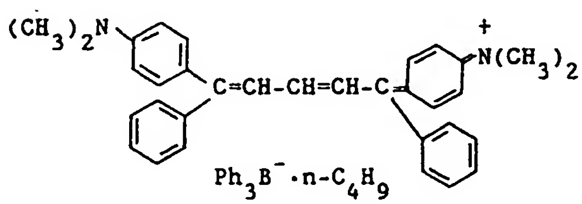
wherein R_1, R_2, R_3 and R_4 independently represent an alkyl, aryl, alkaryl, allyl, aralkyl, alkenyl, alkynyl, alicyclic or saturated or unsaturated heterocyclic group, with the proviso that at least one of R_1, R_2, R_3 and R_4 represents an alkyl group having 1 to 8 carbon atoms.

4. An initiator as claimed in claim 3, wherein the borate anion is selected from triphenylbutyl borate anion and trianisylbutyl borate anion.

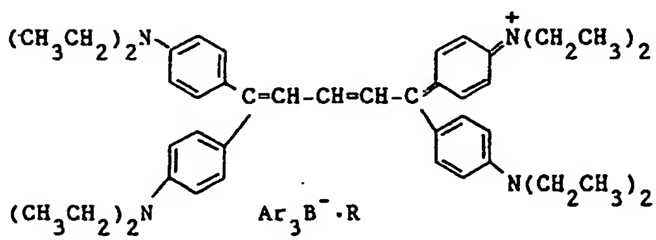
5. An initiator as claimed in any of the claims 1 to 4, wherein the near infrared ray-absorbing cationic dye is selected from the following complexes :



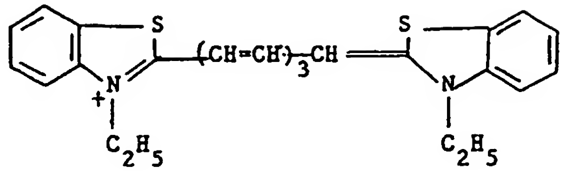
$Ph_3B^- \cdot n\text{-}C_4H_9$



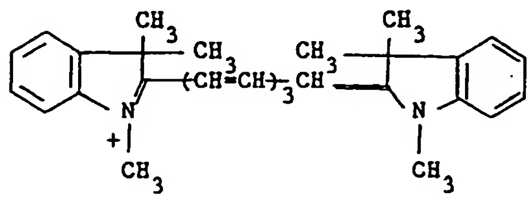
$Ph_3B^- \cdot n\text{-}C_4H_9$



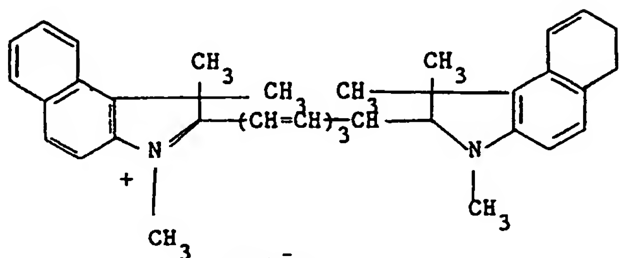
$Ar_3B^- \cdot R$



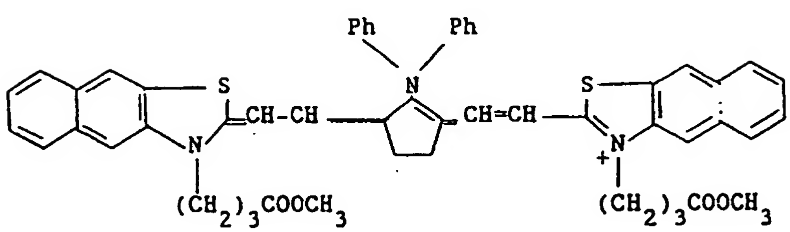
$Ph_3B^- \cdot n\text{-}C_4H_9$



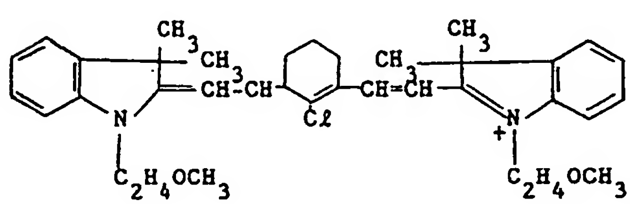
$Ar_3B^- \cdot R$



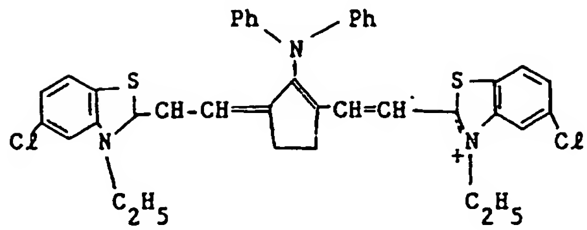
$Ar_3B^- \cdot R$



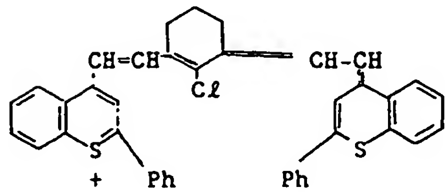
$Ar_3B^- \cdot R$



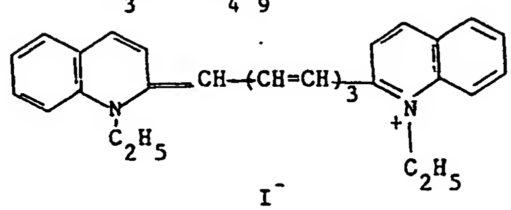
$Ph_3B^- \cdot n\text{-}C_4H_9$

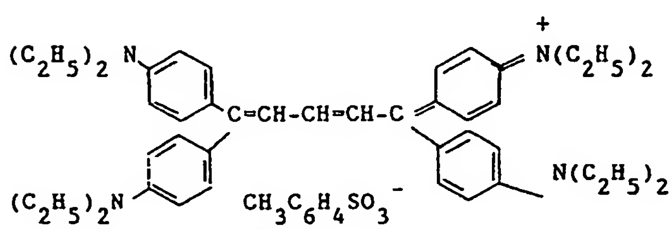


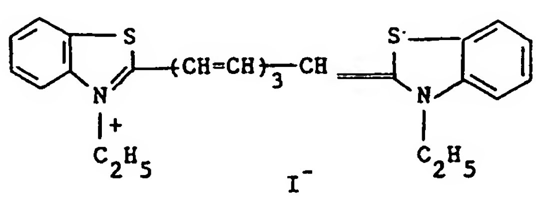
$Ph_3B^- \cdot n\text{-}C_4H_9$

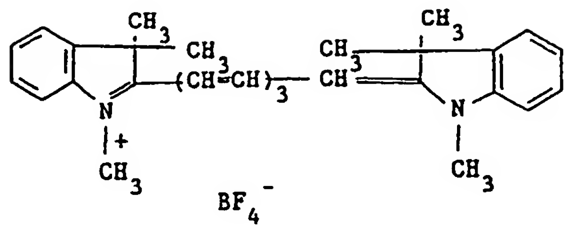


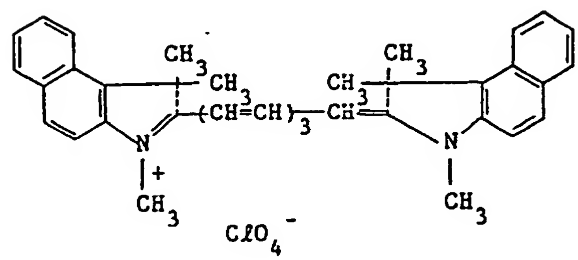
$Ph_3B^- \cdot n\text{-}C_4H_9$

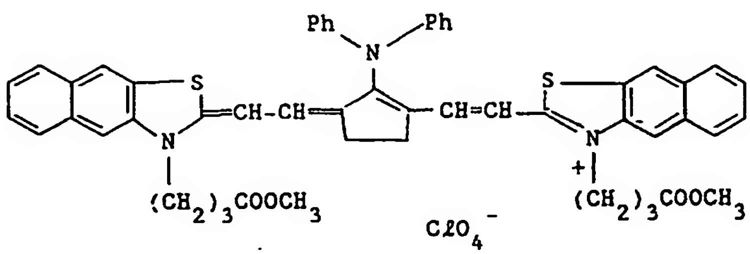


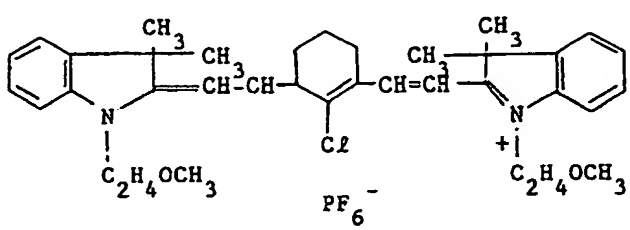


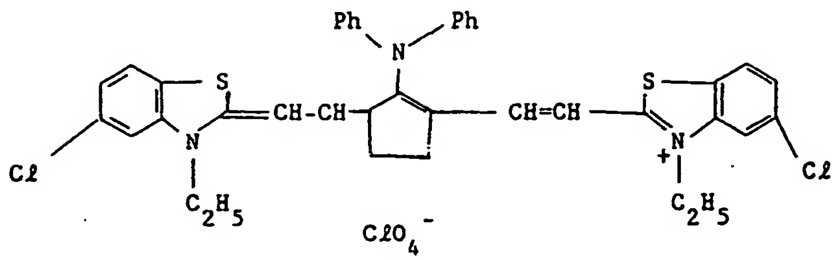


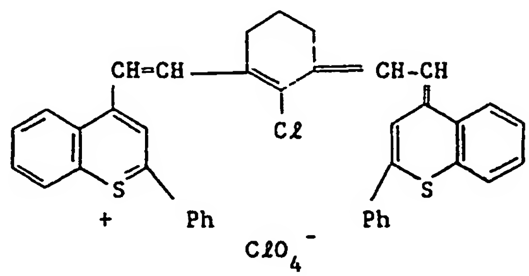


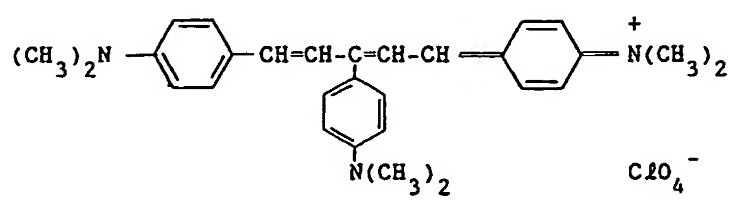


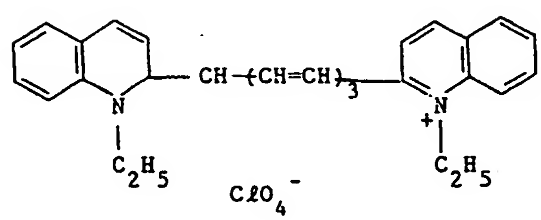


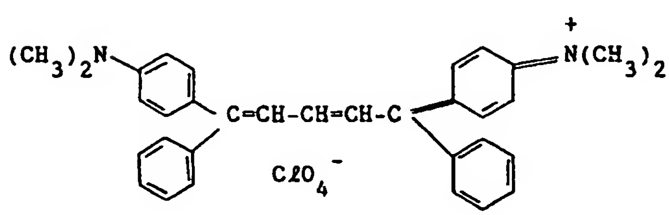


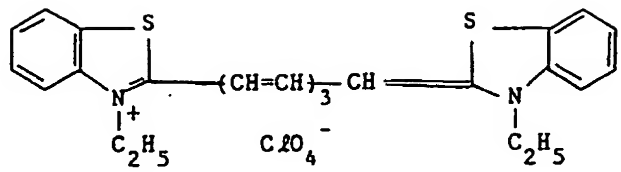


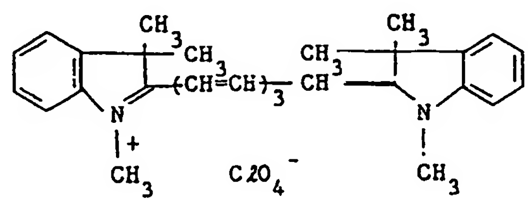




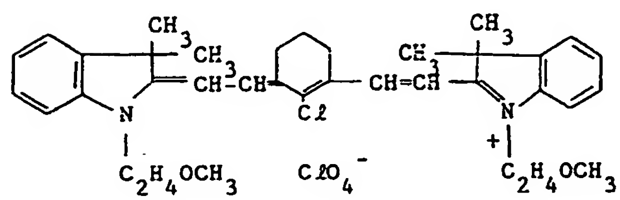








and



in the above formulae, Ph represents phenyl, R represents n-butyl, n-hexyl or n-octyl, and Ar represents phenyl or anisyl.

6. An initiator as claimed in any of the claims 1 to 5, wherein the near infrared ray-absorbing cationic dye is employed in combination with an oxygen scavenger and a chain transfer agent.

7. An initiator as claimed in claim 6, wherein the oxygen scavenger is selected from phosphines, phosphites, phosphonates, stannous salts and other compounds that can be easily oxidized by oxygen.

8. An initiator as claimed in claim 6, wherein the chain transfer agent is selected from N-phenylglycine, N-substituted N-phenylglycines, trimethylbarbituric acid, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, and N,N-dialkylanilines.

9. An initiator as claimed in any of the claims 1 to 8, wherein the boron-containing sensitizer is selected from tetramethylammonium n-butyltriphenyl borate,
tetramethylammonium n-butyltrianisyl borate,
tetramethylammonium n-octyltriphenyl borate,
tetramethylammonium n-octyltrianisyl borate,
tetraethylammonium n-butyltriphenyl borate,
tetraethylammonium n-butyltrianisyl borate,
trimethylhydrogenammonium n-butyltriphenyl borate,
triethylhydrogenammonium n-butyltriphenyl borate,
tetrahydrogeneammonium n-butyltriphenyl borate,
tetramethylammonium tetrabutyl borate and
tetraethylammonium tetrabutyl borate.

10. An initiator as claimed in any of the claims 1 to 8, wherein the organic peroxide is selected from diacyl peroxides such as diacetyl peroxide, dilauroyl peroxide, dibenzoyl peroxide, p,p'-dichlorodibenzoyl peroxide, p,p'-dimethoxydibenzoyl peroxide, p,p'-dimethyldibenzoyl peroxide and p,p'-dinitrodibenzoyl peroxide, hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide and 2,5-

dimethylhexane-2,5-dihydroperoxide, ketone peroxides such as methylethylketone peroxide, and peroxycarbonates such as t-butylperoxide benzoate and 3,3',4,4'-tetra-(t-butylperoxycarbonyl)benzophenone.

11. An initiator as claimed in any of the claims 1 to 10, wherein the boron-containing sensitizer and/or the organic peroxide is contained in an amount of 0.01 to 10 % by weight per %by weight of the near infrared ray-absorbing cationic dye.

12. A process for the polymerization of an ethylenically unsaturated compound, wherein an initiator as claimed in any of the claims 1 to 11 is used.

13. The process as claimed in claim 12, wherein the ethylenically unsaturated compound is selected from acrylic acid and methacrylic acid esters of monohydric alcohols and polyhydric alcohols, and 4-(meth)-acryloyloxyl group-containing aromatic polycarboxylic acids and anhydrides thereof.

14. The process as claimed in claim 12 or 13, wherein the polymerization is initiated with a near infrared ray having a wavelength of at least 700 nm.

15. A photopolymerizable composition for the polymerization with a near infrared ray comprising the near infrared photopolymerization initiator according to any of the claims 1 to 11, and a free-radical addition-polymerizable or crosslinkable compound or a mixture thereof with an organic filler, inorganic filler or composite filler and/or a colorant.

16. A composition as claimed in claim 15, wherein the free-radical addition-polymerizable or crosslinkable compound is an ethylenically unsaturated compound.

17. A composition as claimed in claim 15 or 16, wherein the near infrared ray-absorbing cationic dye is contained in an amount of 0.01 to 10 % by weight based on the ethylenically unsaturated compound.